

Chapter 4

pH AND ALKALINITY

4.1 INTRODUCTION

The subjects of pH and alkalinity are becoming increasingly important as society begins to deal with acidic precipitation. New models developed to analyze effects of alternative controls on inputs of acidity to sensitive aquatic environments use alkalinity as a state variable, then predict pH from alkalinity (Gherini et al., 1984). Earlier models did not contain many of the processes that affect pH, and their predictive capability was adequate for some, but not all, environments (e.g. Henriksen, 1979). More elaborate models now exist which take into account a more complete picture of the constituents that comprise alkalinity in the dilute systems that are at risk from acidic precipitation (organic acids, other non-carbonate weak acids, etc.) and which compute other source-sinks of alkalinity and factors that affect pH (Chen et al., 1984).

4.2 CARBONATE ALKALINITY SYSTEM

The carbonate system is of great importance in lakes, rivers, and estuaries. Carbonate chemistry of natural waters has been described in detail elsewhere (Stumm and Morgan, 1970, 1981; Trussell and Thomas, 1971; Park, 1969; Butler, 1982; Chen and Orlob, 1972, 1975). The carbon dioxide (CO_2) - bicarbonate (HCO_3^-) - carbonate (CO_3^{2-}) equilibrium is the major buffer system in aquatic environments. This equilibrium directly affects the pH, which in turn can affect the biological and chemical constituents of the system. For example, it may become necessary to simulate pH and alkalinity in order to compute the toxicant, un-ionized ammonia (see Chapter 5), or to determine available concentrations of metals (e.g., Gherini et al., 1984).

Since algae use carbon dioxide as a carbon source during photosynthesis, this is a nutrient which can reduce the growth rate when alkalinity is low and other nutrients are high (Goldman, et al., 1972). Most models include a carbonate system representation which calculates the total inorganic carbon (TIC) as the sum of bicarbonate, carbonate, and carbon dioxide. Carbon dioxide is assumed to be produced by respiration and consumed by algal growth. The major source is atmospheric exchange.

The major chemical species considered to constitute alkalinity are dissolved carbon dioxide, bicarbonate, and carbonate ion, together with the hydrogen and hydroxyl ions. Mass balance equations assume that ionic equilibrium exists and calculate carbon inputs and outputs from a pool of total inorganic carbon (TIC). Conversions between different carbon forms are based on stoichiometric equivalents. The carbon dioxide form is involved in most of the important processes, including surface reaeration, respiration, excretion, algal uptake, and organic decay reactions. However, dissolved carbon dioxide combines with water to form carbonic acid, which, in turn, dissociates to bicarbonate ion, carbonate ion, and hydrogen ion. Since the dissociation reactions occur very rapidly in comparison to the other biological and chemical processes, dissolved carbon is modeled as the sum of $\text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-}$, and is referred to as total inorganic carbon (TIC).

Dissolved inorganic carbon is derived from several sources. These include surface reaeration; respiration by fish, zooplankton, benthic animals, and algae; soluble excretion by fish, zooplankton, and benthic animals; and the decay of organic matter in the form of detritus, sediment, and sewage BOD. Dissolved carbon is removed by assimilation during algal photosynthesis.

Conceptually, the mass balance equation defining these relationships for the EAM model (Tetra Tech, 1980) is expressed as follows:

$$\begin{aligned}
(\text{vol}) \frac{d(\text{TIC})}{dt} = & (\text{vol}) \left[(\text{det}) (K_{\text{det}}) (C_{\text{det}}) + (\text{sed}) (K_{\text{sed}}) (C_{\text{sed}}) \right. \\
& + \sum_{i=1}^{n_f} \sum_{j=1}^{n_l} (\text{fish}_{ij} \cdot \text{Fr}_{ij} \cdot C_{\text{fish}}) + (\text{ben}) (\text{Br}) (C_{\text{ben}}) \\
& + \sum_{i=1}^{n_z} (\text{zoo}_i \cdot \text{Zr}_i \cdot C_{\text{zoo}}) + \sum_{i=1}^{n_a} (\text{alg}_i \cdot \text{Ar}_i \cdot C_{\text{alg}}) \\
& + \sum_{i=1}^{n_f} \sum_{j=1}^{n_l} (\text{fish}_{ij} \cdot \text{Fdex}_i \cdot C_{\text{fish}}) \\
& + \sum_{i=1}^{n_z} (\text{zoo}_i \cdot \text{Zdex}_i \cdot C_{\text{zoo}}) + (\text{ben}) (\text{Bdex}) (C_{\text{ben}}) \\
& - \sum_{i=1}^{n_a} (\text{alg}_i \cdot \text{Ag}_i \cdot C_{\text{alg}}) \\
& + (\text{BOD}) (K_{\text{BOD}}) (C_{\text{BOD}}) \Big] \\
& + (R_{\text{CO}_2}) (CO_{2\text{sat}} - CO_2) (\text{Area}) \tag{4-1}
\end{aligned}$$

= detritus decay + sediment decay + fish respiration
 + benthic animal respiration + zooplankton respiration
 + algal respiration + fish excretion + zooplankton excretion
 + benthic animal excretion - algal assimilation
 + BOD decay + surface reaeration.

Although Equation (4-1) is a substantially complete picture of TIC dynamics in an aquatic system, most models do not contain the same degree of complexity. However, whether multi-compartmented or few compartments, the general aspects of the process are modeled similarly. Also, the inputs and outputs can be based on CO_2 with suitable stoichiometric conversions (e.g., Di Toro and Connolly, 1980) rather than TIC.

Surface reaeration of CO_2 from atmospheric sources is done in a way similar to oxygen (Section 3.2). However, only minimal effort to measure

CO₂ reaeration is necessary and literature values have been used (Emerson, 1975; Liss, 1973). Reaeration occurs only at the surface of the water body, and is a function of the carbon dioxide saturation level. The saturation concentration is a function of the water temperature as it affects the Henry's law constant (K_H) for computing CO_{2sat}:

$$CO_{2sat} = K_H pCO_2 \quad (4-2)$$

where pCO₂ is the partial pressure of CO₂ in the atmosphere (generally 0.00033 atmospheres is used) and

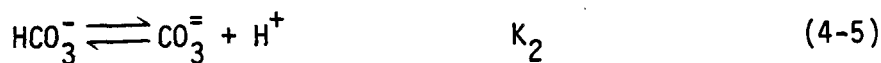
$$K_H = M_{CO_2} 10^{\left[\frac{2385.73}{T_K} - 14.0184 + 0.0152642 T_K \right]} \quad (4-3)$$

where M_{CO₂} = 44,000 mg/mole, CO₂

T_K = temperature in K = 273.15 + °C

K_H = Henry's law constant, mg/(liter·atm)

After computing the total inorganic carbon according to the mass balance in Equation (4-1), the dissolved carbon dioxide concentration is calculated using relationships derived from the equilibrium constants of the dissociation reactions. The reactions involved are:



where the equilibrium constants are defined as

$$K_1 = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \quad (4-7)$$

$$K_2 = \frac{[\text{CO}_3^{=}] [\text{H}^+]}{[\text{HCO}_3^-]} \quad (4-8)$$

$$K_w = [\text{H}^+] [\text{OH}^-] \quad (4-9)$$

The equilibrium constants K_1 , K_2 , and K_w vary with temperature according to the following relationships (Tetra Tech, 1979):

$$K_1 = 10^{\left[14.8435 - 0.032786 T_K - (3404.71/T_K) \right]} \quad (4-10)$$

$$K_2 = 10^{\left[6.498 - 0.02379 T_K - (2902.39/T_K) \right]} \quad (4-11)$$

$$K_w = 10^{\left[35.3944 - 0.00835 T_K - (5242.4/T_K) - 11.826 \log(T_K) \right]} \quad (4-12)$$

In a carbonate system, the alkalinity (alk) is calculated according to the mass balance equation:

$$\text{alk} = \text{alkalinity} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{=}] + [\text{OH}^-] - [\text{H}^+] \quad (4-13)$$

Other processes can affect alkalinity in aquatic systems. Addition of acids and nitrification reduce alkalinity, and uptake of nitrate by algae increases alkalinity. Because of the magnitude of the ammonia concentration in waters receiving municipal effluents, nitrification can affect alkalinity substantially, generating 2 equivalents of acid (H^+) per equivalent of ammonia oxidized (see Section 3.4). Similarly in eutrophic waters, nitrate uptake can increase alkalinity by the production of approximately 1 equivalent of base (OH^-) per equivalent of nitrate taken up by plant cells. These corrections would be of consequence in low alkalinity waters (less than 200 $\mu\text{eq/l}$), and would be applied to Equation (4-13).

Once the total inorganic carbon and alkalinity have been determined using the mass balance equations (4-1, 4-13), the hydrogen ion concentration

can be calculated by trial and error solution of the following relationship:

$$\text{alk} = [\text{TIC}] \frac{1 + \frac{2K_2}{[\text{H}^+]}}{1 + \frac{[\text{H}^+]}{K_1} + \frac{K_2}{[\text{H}^+]}} + \frac{K_{ws}}{[\text{H}^+]} - [\text{H}^+] \quad (4-14)$$

After $[\text{H}^+]$ is determined, it is substituted into the expression for CO_2 , which can then be solved directly for the dissolved CO_2 concentration:

$$\text{CO}_2 = \frac{[\text{TIC}]}{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 \cdot K_2}{[\text{H}^+]^2}} \quad (4-15)$$

Not all models compute inorganic carbon species or pH. Generally these computations have been made primarily in lake systems where they are of significance in acid precipitation or are used for additional model verification as in Di Toro and Connolly (1980). In all cases, the formulations are based on the above derivations, although the computation details may differ from model to model. Water quality models that contain the CO_2 , alkalinity, pH formulations include those discussed in the following references:

Smith, 1978	WQRRS
Thomann <u>et al.</u> , 1974	LAKE-3
Di Toro and Connolly, 1980	Lake Erie Model
Scavia, <u>et al.</u> , 1976	Lake Ontario Model
Tetra Tech, 1980	EAM
WES, 1982	CE-QUAL-R1

4.3 EXTENDED ALKALINITY APPROACH

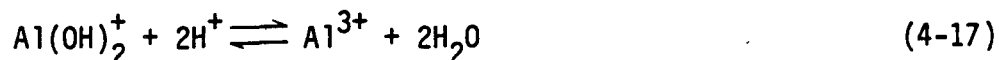
4.3.1 Definition of Extended Alkalinity

The mass balance equation (4-13) has ignored several H^+ -ion acceptors, and is appropriate in many instances. In very low alkalinity waters,

however, the concentration of these neglected H^+ -ion acceptors can be significantly large. The neglected H^+ -ion acceptors include organic substances with carboxyl and phenolic hydroxyl groups, for example:



and the monomeric aluminum species and their complexes, for example,



and



An extended alkalinity relationship would include the alkalinity associated with water itself, the carbonate system, the monomeric aluminum system and its organic complexes, and dissolved organic acid anions. The dissolved organic carbon alkalinity can be represented by a triprotic (H_3R_1) and/or monoprotic (HR_1) model organic acid with fixed dissociation constants and a fixed number of acid-base functional groups per unit mass of carbon (eq/mgC). The components of the total alkalinity, as represented by the H^+ -ion acceptors, are given below:

$$Alk = \underbrace{Alk_{H_2O}}_{\text{water}} + \underbrace{Alk_C}_{\text{carbonate system}} + \underbrace{Alk_{R_1} + Alk_{R_2}}_{\text{organic acids}} + \underbrace{Alk_{Al} + Alk_{Al \cdot O}}_{\text{aluminum system}} \quad (4-19)$$

where

$$Alk_{H_2O} = [OH^-] - [H^+] \quad (4-20)$$

$$Alk_C = [HCO_3^-] + 2[CO_3^{2-}] \quad (4-21)$$

$$Alk_{R_1} = [H_2R_1^-] + 2[HR_1^{2-}] + 3[R_1^{3-}] \quad (4-22)$$

$$Alk_{R_2} = [R_2^-] \quad (4-23)$$

$$Alk_{A1} = [Al(OH)^{2+}] + 2[Al(OH)_2^+] + 3[Al(OH)_3^0] + 4[Al(OH)_4^-] \quad (4-24)$$

$$Alk_{A1.0} = 3[Al R_1] + [Al R_2^{2+}] + 2[Al(R_2)_2^+] + 3[Al(R_2)_3] \quad (4-25)$$

An alternative representation of solution-phase alkalinity, which is mathematically equivalent to the above is given as follows,

$$Alk = \sum_k Z_k N_k = \sum C_B - \sum C_A \quad (4-26)$$

where $\sum C_B$ = the sum of the base cations

$$= 2[C_a^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+] + [NH_4^+] \quad (4-27)$$

$\sum C_A$ = the sum of the strong acid anions

$$= 2[SO_4^{2-}] + [NO_3^-] + [Cl^-] \quad (4-28)$$

The derivation is based on the mass balance equation and the solution electroneutrality condition. Figure (4-1) shows the equivalence for lakes in the State of Washington.

4.3.2 Modeling Extended Alkalinity

The concept of extended alkalinity has been incorporated in a model called PHCALC. This model was developed primarily for the ILWAS model (Tetra Tech, 1983), and was later modified into an interactive FORTRAN program to compute any one of the following options: pH, alkalinity, total inorganic carbon (TIC) and "solution equilibration". The solution equilibration approach is similar to the approach for pH, except that alkalinity can be adjusted for gibbsite precipitation or dissolution. Table 4-1 shows the list of required parameters for any given option.

All the concentrations on the left-hand-side of Equations (4-20) through (4-25) can be expressed in terms of ionization fractions and

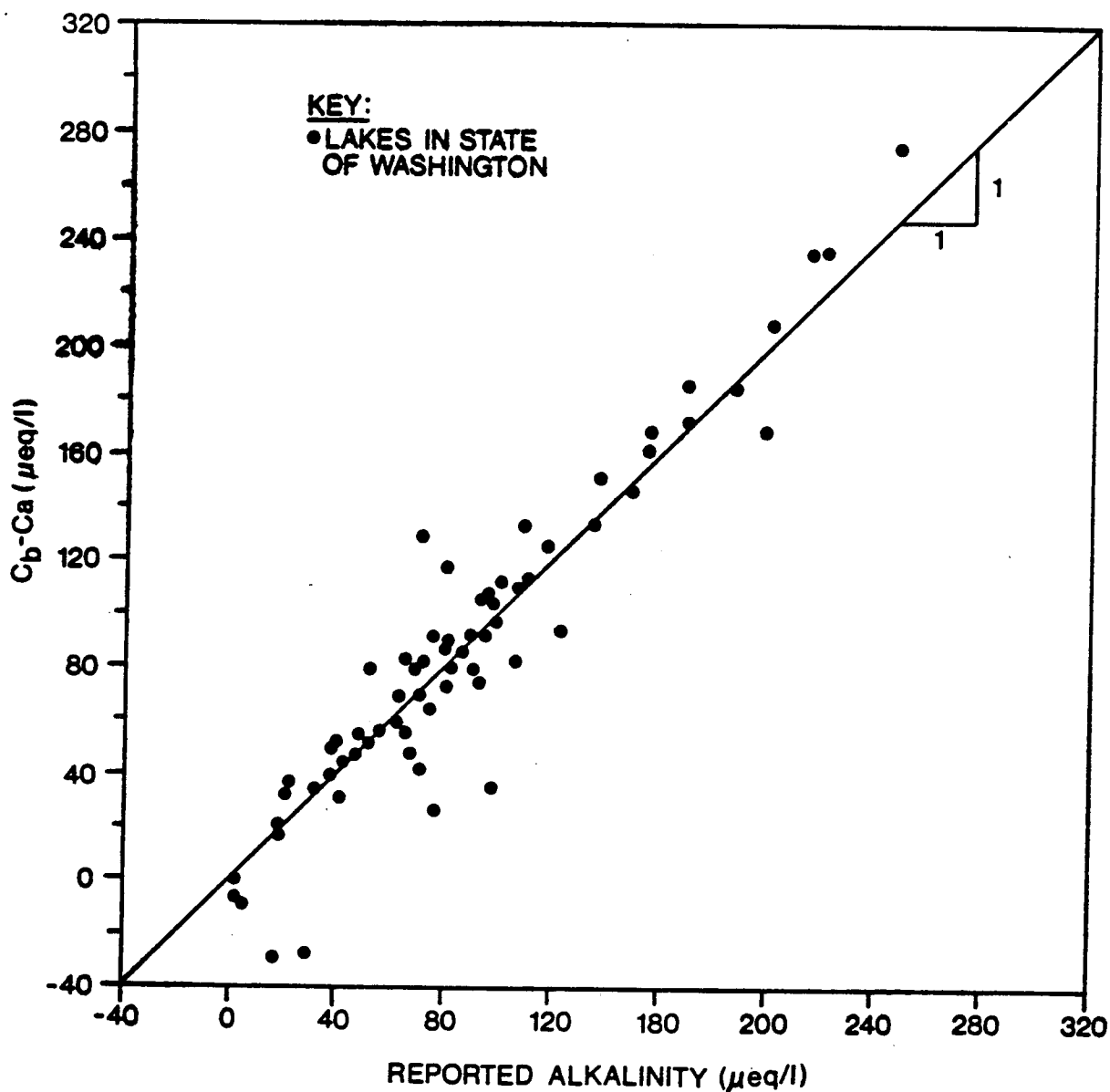


Figure 4-1. $[\Sigma C_B - \Sigma C_A]$ plotted against reported alkalinity
(from Gherini *et al.*, 1984).

temperature-dependent dissociation constants. Fluoride and sulfate concentrations are required for the determination of their complexations with aluminum.

4.3.3 Equilibrium Constants and Solubility Products

The equilibrium constants used in PHCALC are obtained by first expressing a thermodynamic temperature dependence for a related constant, K_i :

TABLE 4-1. OPTIONS AND THEIR REQUIRED INPUT PARAMETERS FOR PHCALC

Options*	Parameters Required to be Specified
pH	Alk, TIC or EQ ₁ , Al _T , OAC ₁ , OAC ₂ , F, SO ₄ ²⁻ , T
Alk	pH, TIC or EQ ₁ , Al _T or EQ ₂ , OAC ₁ , OAC ₂ , F, SO ₄ ²⁻ , T
TIC	pH, Alk, Al _T , or EQ ₂ , OAC ₁ , OAC ₂ , F, SO ₄ ²⁻ , T
EQ	Alk, TIC or EQ ₁ , Al _T , EQ ₂ , OAC ₁ , OAC ₂ , F, SO ₄ ²⁻ , T

Definition of Parameters:

Alk	alkalinity
TIC	total inorganic carbon
EQ	equilibration of a solution with Al(OH) ₃
Al _T	total aluminum
OAC ₁	total organic acid (1)
OAC ₂	total organic acid (2)
F	fluoride concentration
SO ₄ ²⁻	sulfate concentration
T	temperature, °C
EQ ₁	ratio of TIC to air-equilibrated TIC (specified for open system)
EQ ₂	-log (Ksp) for Al(OH) ₃ mineral or one of the following minerals for the equilibration with gibbsite
	AG - amorphous gibbsite (pK _{sp} = 31.19)
	MG - microcrystalline gibbsite (pK _{sp} = 32.64)
	NG - natural gibbsite (pK _{sp} = 33.22)
	SG - synthetic gibbsite (pK _{sp} = 33.88)

*Options are the parameters to be computed

$$\log_{10} K_i = a + \frac{b}{T} + cT + d\log_{10} T \quad (4-29)$$

The constants a, b, c and d are given as follows:

	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>Reference</u>
K_w	6.0875	-4470.99	-0.01706	0	Stumm & Morgan, 1981
K_1	545.56	-17052	0.12675	-215.21	Loewenthal & Marais, 1978
K_2	-6.498	2902.39	0.02379	0	Loewenthal & Marais, 1978
K_H	-14.0184	2385.73	0.0152642	0	Stumm & Morgan, 1981

K_w , K_1 , and K_2 are dimensionless while K_H is in moles liter⁻¹ atm⁻¹. K_H has to be multiplied by RT to convert to a dimensionless form. R is the universal gas constant and T is the absolute temperature in degrees Kelvin in the range of 273 K to 313 K.

The solubility products used in the equilibration with gibbsite were shown earlier in Table 4-1.

4.4 SUMMARY

Two approaches have been presented for the relationship of total inorganic carbon, alkalinity and pH. For waters with low dissolved organic carbon (with little color) and high alkalinity ($\text{alk} \geq 200 \mu\text{eq/l}$), the conventional alkalinity definition is recommended. For waters with high dissolved organic carbon and waters with $\text{alk} < 200 \mu\text{eq/l}$ where the alkalinities contributed by aluminum and organic acids are no longer negligible, the extended alkalinity approach is recommended. The equivalence between the expression $\text{Alk} = \Sigma C_B - \Sigma C_A$ and the extended alkalinity definition provides a convenient tool in alkalinity evaluation.

4.5 REFERENCES

Butler, J.N. 1982. Carbon Dioxide Equilibria and their Applications. Addison-Wesley Pub. London. 259 p.

Chen, C.W., and G.T. Orlob. 1972. Ecological Simulation for Aquatic Environments, Report to Office of Water Resources Research OWRR C-2044, Water Resources Engineers Inc., Walnut Creek, California.

Chen, C.W., and G.T. Orlob. 1975. Ecologic Simulation of Aquatic Environments. Systems Analysis and Simulation in Ecology, Vol. 3, B.C. Patten, (ed.). Academic Press, New York, N.Y. pp. 476-588.

Chen, C.W., S.A. Gherini, J.D. Dean, R.J.M. Hudson, and R.A. Goldstein. 1984. Development and Calibration of the Integrated Lake-Watershed Acidification Study Model. In Modeling of Total Acid Precipitation Impacts. J.L. Schnoor (Ed.), Butterworth, Boston, Mass.

Di Toro, D.M., and J.P. Connolly. 1980. Mathematical Models of Water Quality in Large Lakes Part 2: Lake Erie, EPA-600/3-80-065, U.S. Environmental Protection Agency, Duluth, Minnesota.

Emerson, S. 1975. Gas Exchange Rates in Small Canadian Shield Lakes. Limnol. Oceanogr. 20:754-761.

Gherini, S.A., C.W. Chen, L. Mok, R.A. Goldstein, R.J.M. Hudson, and G.F. Davis. 1984. The ILWAS Model: Formulation and Application. In the Integrated Lake-Watershed Acidification Study. 4: Summary of Major Results. EPRI EA-3221. p. 7-1 to 7-46.

Goldman, J.C., D.B. Porcella, E.J. Middlebrooke, and D.F. Toerien. 1972. Review Paper: The Effect of Carbon on Algal Growth: Its Relationship to Eutrophication. Water Res. 6:637-679.

Henriksen, A. 1979. A Simple approach For Identifying and Measuring Acidification in Freshwater. Nature, 278, 542.

Liss, P.S. 1973. Processes of Gas Exchange Across an Air-Water Interface. Deep-Sea Res. 20: 221-238.

Loewenthal, R.E., and G.V.R. Marais. 1978. Carbonate Chemistry of Aquatic Systems: Theory and Application. Volume 1. Ann Arbor Science, Michigan.

Parks, P.K. 1969. Oceanic CO₂ System: An Evaluation of Ten Methods of Investigation: 179-186.

Scavia, D., B.J. Eadie, and A. Robertson. 1976. An Ecological Model for Lake Ontario Model Formulation, Calibration, and Preliminary Evaluation. NOAA Technical Report ERL 371-GLERL 12. NOAA. Boulder Colorado. 63 p.

Smith, D.I. 1978. WQRRS, Generalized Computer Program for River-Reservoir Systems. User's Manual 401-100, 100A: U.S. Army Corps of Engineers, Hydrologic Engineering Center (HEC), Davis, California. 210 pp.

Snoeyink, V.L., and D. Jenkins. 1980. Water Chemistry. New York. John Wiley & Sons.

Stumm, W., and J.J. Morgan. 1970. Aquatic Chemistry. (New York: Wiley-Interscience).

Stumm, W., and J.J. Morgan. 1981. Aquatic Chemistry, 2nd Ed., Wiley, New York.

Tetra Tech, Inc. 1979. Methodology for Evaluation of Multiple Power Plant Cooling System Effects, Volume II: Technical Basis for Computations. Electric Power Research Institute, Report EPRI EA-1111.

Tetra Tech, Inc. 1980. Methodology for Evaluation of Multiple Power Plant Cooling System Effects, Volume V. Methodology Application to Prototype-Cayuga Lake. Electric Power Research Institute, Report EPRI EA-1111.

Tetra Tech, Inc. 1983. The Integrated Lake-Watershed Acidification Study, Volume 1: Model Principles and Application Procedures. Electric Power Research Institute. Report EPRI EA-3221.

Thomann, R.V., D.M. Di Toro, R.P. Winfield, and D.J. O'Connor. 1975. Mathematical Modeling of Phytoplankton in Lake Ontario. I. Model Development and Application. EPA-660/3-75-005. USEPA, Corvallis, Oregon, 97330. 177 p.

Trussell, R.R., and J.F. Thomas. 1971. A Discussion of the Chemical Character of Water Mixtures. J. American Water Works Assoc. 63(1), 49.

Chapter 5

NUTRIENTS

5.1 INTRODUCTION

Certain elements are referred to as nutrients because they are essential to the life processes of aquatic organisms. The major nutrients of concern are carbon, nitrogen, phosphorus, and silicon. Silicon is important only for diatoms, one of the major components of the algal community. Other micronutrients such as iron, manganese, sulphur, zinc, copper, cobalt, and molybdenum are also important. However, these latter nutrients are not considered in water quality models because they are required only in trace amounts and they are usually present in quantities adequate to meet the biochemical requirements of the organisms.

Nutrients are important in water quality modeling for several reasons. For example, nutrient dynamics are critical components of eutrophication models since nutrient availability is usually the main factor controlling algal blooms. Algal growth is typically limited by either phosphorus or nitrogen, with the exception of diatoms which are often silicon limited. Some blue-green algae can fix nitrogen and are therefore not limited by nitrogen. Carbon is usually available in excess although in some cases it may also be limiting. Carbon is also important because of its role in the pH-carbonate system, as discussed in Chapter 4.

Nitrogen is important in water quality modeling for reasons other than its role as a nutrient. For example, the oxidation of ammonia to nitrate during the nitrification process consumes oxygen and may represent a significant portion of the total BOD. Also, high concentrations of unionized ammonia can be toxic to fish and other aquatic organisms.

5.2 NUTRIENT CYCLES

Nutrients are present in several different forms in aquatic systems:

- dissolved inorganic nutrients
- dissolved organic nutrients
- particulate organic (detrital) nutrients
- sediment nutrients
- biotic nutrients (algae, aquatic plants, zooplankton, fish, benthic organisms)

Only the dissolved inorganic forms are available for algal growth. These include dissolved CO_2 , ammonia, nitrite, and nitrate nitrogen, orthophosphate, and dissolved silica.

Each nutrient undergoes continuous recycling between the major forms listed above. For example, dissolved inorganic nutrients are removed from the water column by algae and aquatic plants during photosynthesis. These nutrients are distributed to the other aquatic organisms through the food web. Dissolved inorganic nutrients are returned to the water through the soluble excretions of all organisms, the decomposition of organic detritus and sediments, and the hydrolysis of dissolved organic nutrients. In addition, dissolved CO_2 and N_2 gases exchange with the atmosphere. Suspended particulate nutrients are generated through the particulate excretions of aquatic animals and the death of planktonic organisms. Organic detritus and phytoplankton which settle to the bottom contribute to the sediment nutrients. Decomposition of suspended organic detritus and organic sediment releases both dissolved organic and dissolved inorganic nutrients to the water.

Many of the above interactions are shown in Figure 5-1 for carbon, nitrogen, and phosphorus and in Figure 5-2 for silicon. Figures 5-3 and 5-4 present more detailed descriptions of the nitrogen and phosphorus cycles.

In addition to the internal recycling of nutrients within the waterbody, nutrients are also introduced through wasteloads (both point and nonpoint sources), river or tributary inflows, runoff, and atmospheric precipitation.

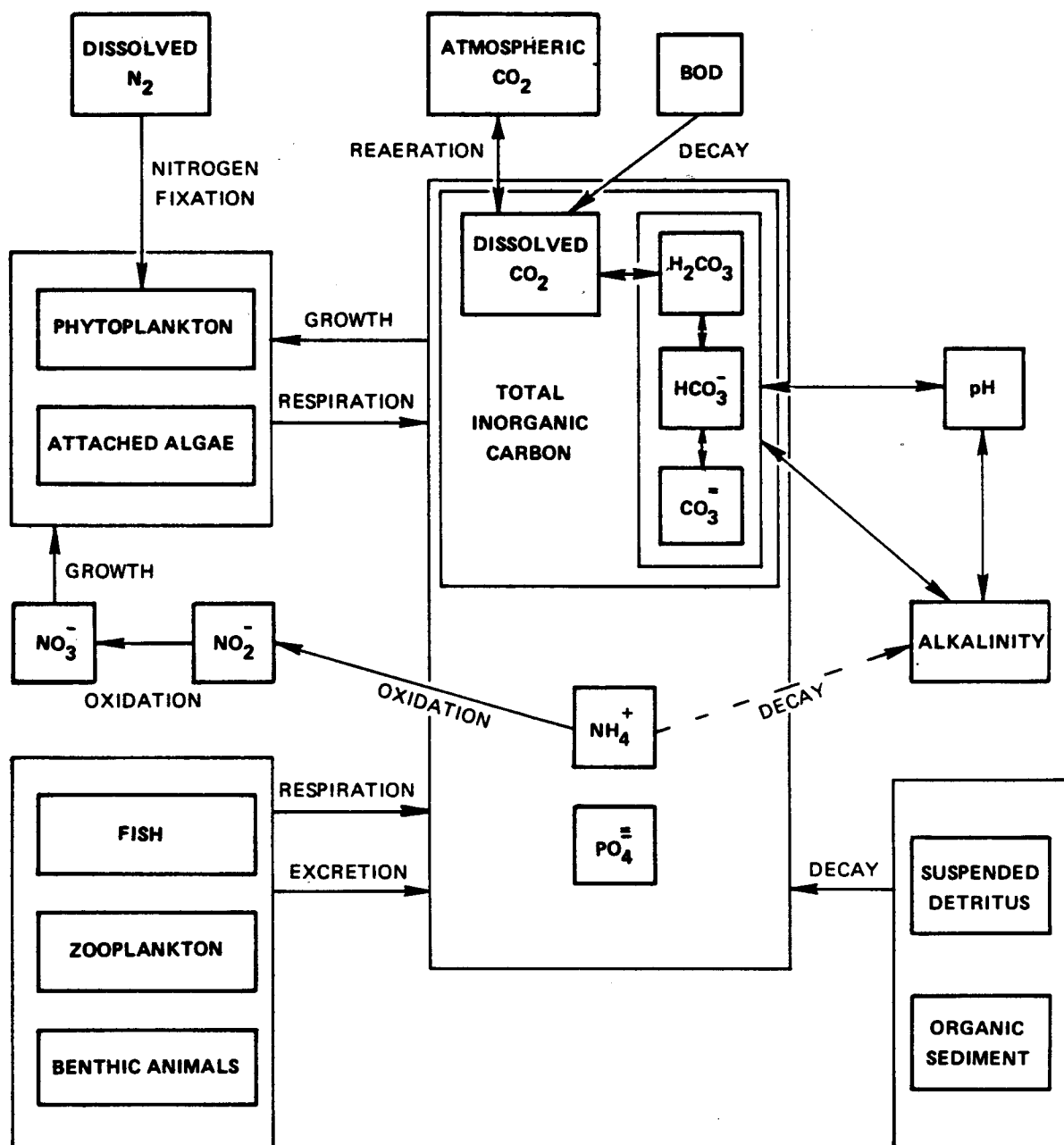


Figure 5-1. Nutrient interactions for carbon, nitrogen, and phosphorus (from Tetra Tech, 1979).

5.3 GENERAL MODELING APPROACH FOR ALL NUTRIENTS

Nutrient dynamics are governed by the following processes:

- dissolved inorganic nutrients
 - photosynthetic uptake
 - excretion
 - chemical transformations (e.g., oxidation of NH_3)
 - hydrolysis of dissolved organic nutrients
 - detritus decomposition
 - sediment decomposition and release
 - external loading

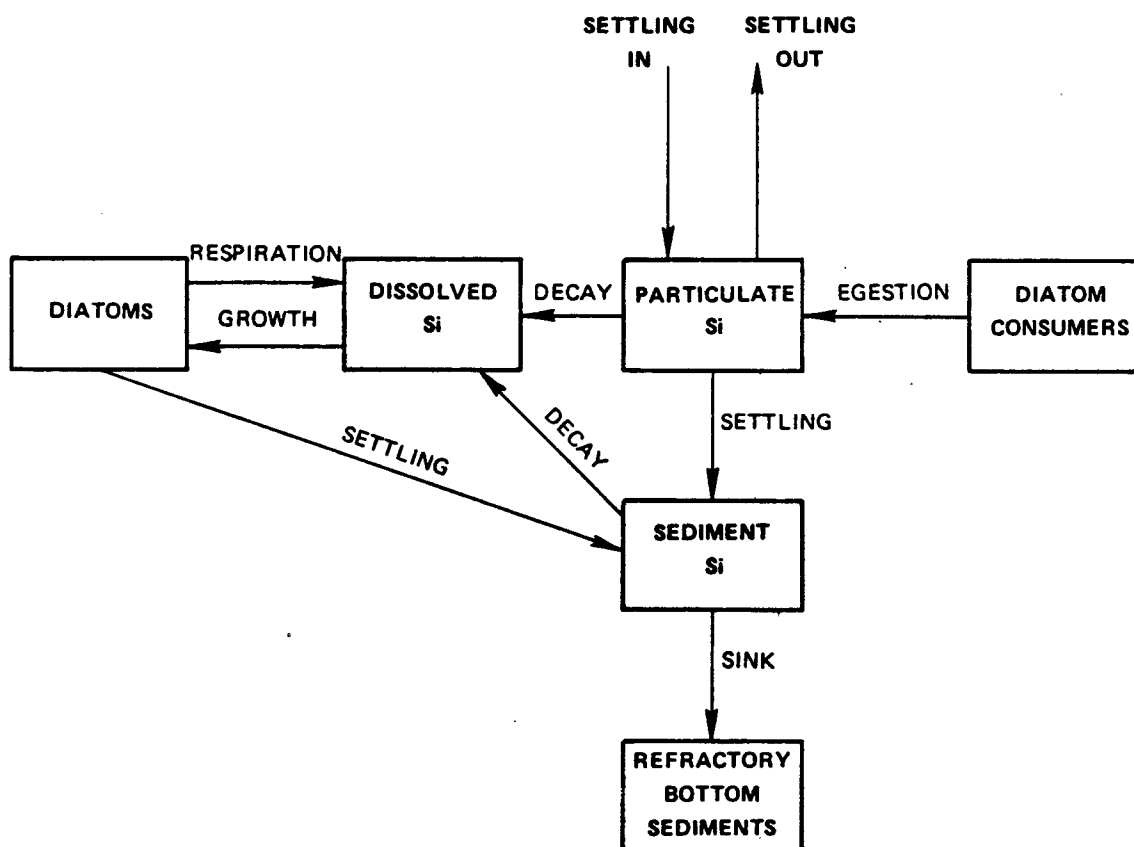


Figure 5-2. Nutrient interactions for silica (from Tetra Tech, 1979).

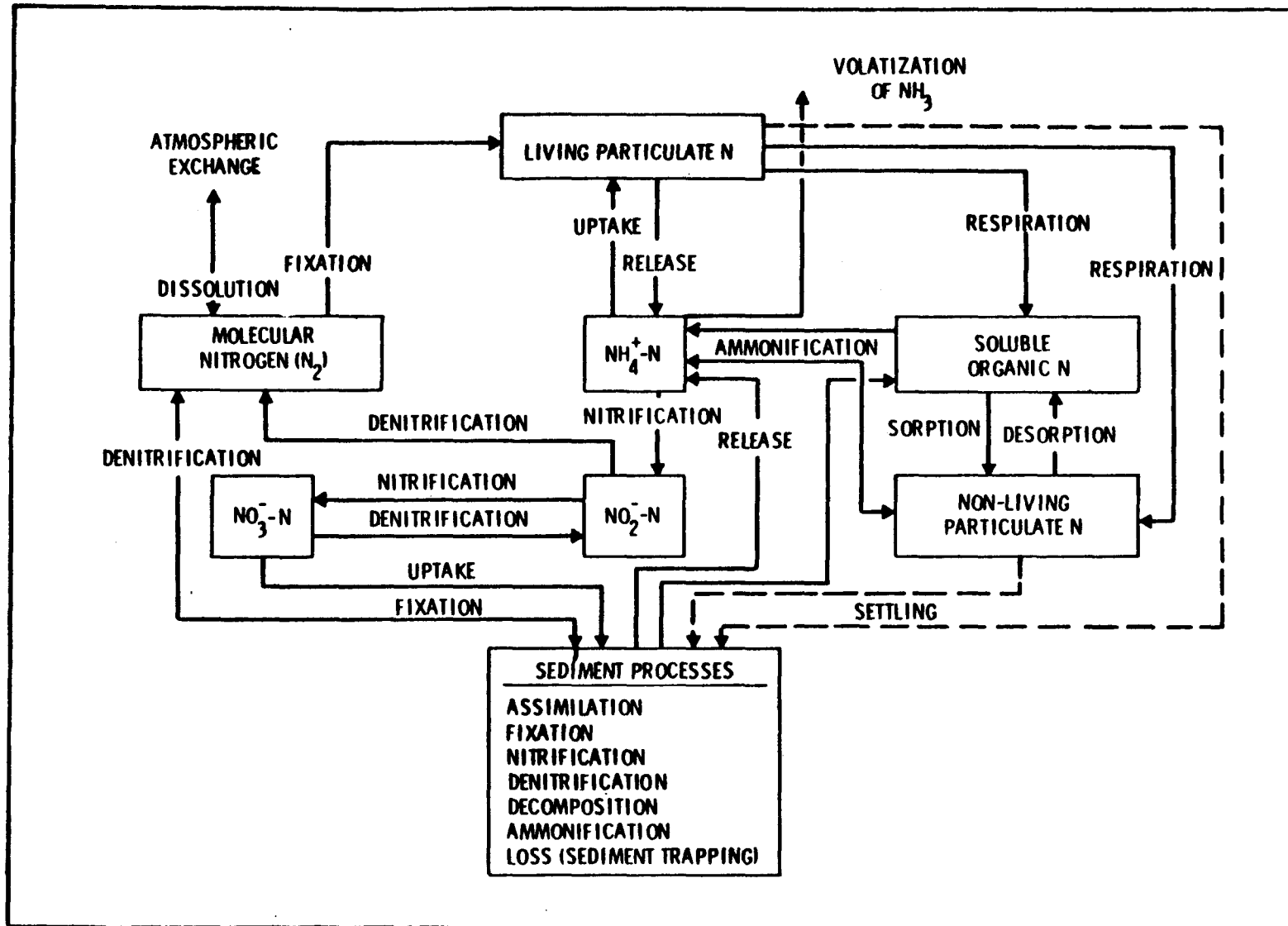


Figure 5-3. Nitrogen cycle (from Baca and Arnett, 1976).

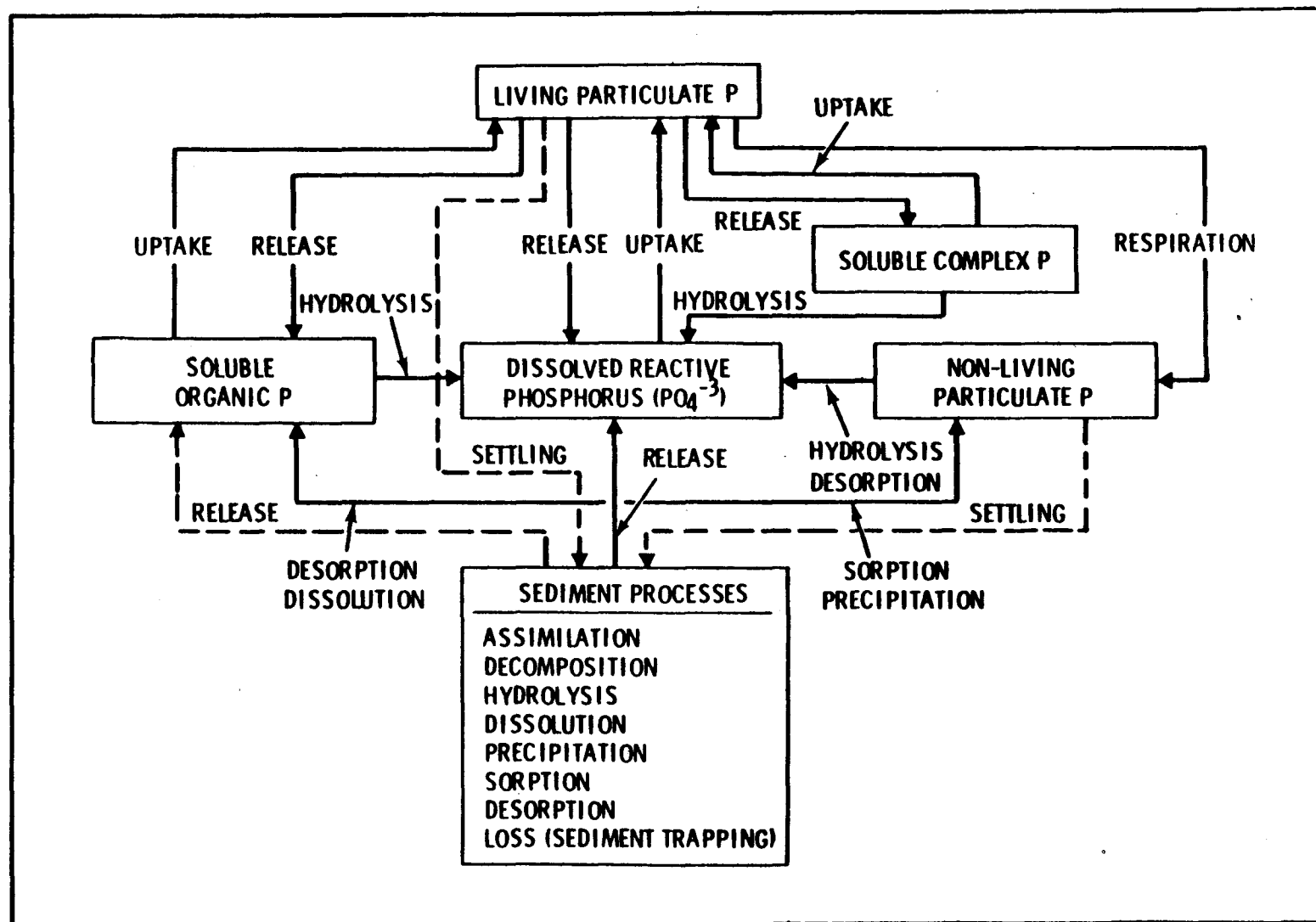


Figure 5-4. Phosphorus cycle (from Baca and Arnett, 1976).

- dissolved organic nutrients
 - excretion
 - hydrolysis
 - detritus decomposition
 - sediment decomposition and release
 - external loading

- particulate organic nutrients
 - particulate excretions
 - plankton mortality
 - decomposition
 - settling
 - zooplankton grazing
 - external loading

- sediment nutrients
 - detritus settling
 - algal settling
 - sediment decomposition and release

Only processes affecting the abiotic forms of nutrients are discussed in this chapter since the biotic components of water quality models are discussed in Chapters 6 (Algae) and 7 (Zooplankton).

Nutrients are modeled by using a system of coupled mass balance equations describing each nutrient compartment and each process listed above, plus the transport processes of advection and dispersion discussed in Chapter 2. The general equations for each nutrient, omitting the transport and external loading terms, can be expressed as follows:

dissolved inorganic nutrients:

$$\begin{aligned} \frac{dS}{dt} = & -V_s + f_1 e_s + K_1 S' - K_2 S + K_{org} S_{org} + f_2 K_{det} S_{det} \\ & + f_3 K_{sed} S_{sed} \end{aligned} \quad (5-1)$$

dissolved organic nutrients:

$$\begin{aligned} \frac{dS_{org}}{dt} = & (1 - f_1) e_s - K_{org} S_{org} + (1 - f_2) K_{det} S_{det} \\ & + (1 - f_3) K_{sed} S_{sed} \end{aligned} \quad (5-2)$$

particulate organic nutrients:

$$\frac{dS_{det}}{dt} = e_p + M_p - K_{det} S_{det} - K_s S_{det} - G_z \quad (5-3)$$

sediment nutrients:

$$\frac{dS_{sed}}{dt} = K_s S_{det} + A_s - K_{sed} S_{sed} \quad (5-4)$$

- where S = dissolved inorganic nutrient concentration, mass/volume
 S' = another inorganic form of the nutrient which decays to the form S (e.g., NH_3 NO_3), mass/volume
 S_{org} = dissolved organic nutrient concentration, mass/volume
 S_{det} = suspended particulate organic nutrient concentration, mass/volume
 S_{sed} = organic sediment nutrient concentration, mass/volume
 K_1 = transformation rate of S' into S, 1/time
 K_2 = transformation rate of S into some other dissolved inorganic form of the nutrient, 1/time
 K_{org} = hydrolysis rate of dissolved organic nutrient, 1/time
 K_{det} = decomposition rate of particulate organic nutrient, 1/time
 K_{sed} = decomposition rate of organic sediment nutrient, 1/time
 K_s = settling rate for particulate organic nutrient, 1/time
 V_s = photosynthetic uptake rate for nutrient S, mass/volume-time
 e_s = soluble excretion rate of nutrient by all organisms, mass/volume-time
 f_1 = fraction of soluble excretions which are inorganic

- f_2 = fraction of detritus decomposition products which are immediately available for algal uptake
- f_3 = fraction of sediment decomposition products which are immediately available for algal uptake
- e_p = particulate excretion rate of nutrient by all animals, mass/volume-time
- M_p = total rate of plankton mortality, mass/volume-time
- G_z = detritus grazing rate by zooplankton, mass/volume-time
- A_s = algal settling rate to sediment, mass/volume-time

Note that all of the transformations between the various abiotic nutrient compartments are described by first-order kinetics. This approach is used in almost all water quality models. Nutrient models differ primarily in the specific nutrients simulated (i.e., C, N, P, and Si) and in the number of compartments used to describe each nutrient cycle (i.e., dissolved inorganic forms such as NH_3 , NO_2 , and NO_3 ; dissolved organic components; particulate organic components; sediments; and biotic components such as algae and zooplankton).

For example, many models omit carbon since it does not limit algal growth in most situations. Silicon is generally modeled only when diatoms are simulated as a separate phytoplankton group.

The nutrient cycles are often simplified by combining or omitting some of the forms described above. For example, many models do not simulate sediment nutrients explicitly with a mass balance equation such as Equation (5-4). Instead, user-specified sediment fluxes are specified in Equations (5-1) and (5-2). Dissolved organic nutrients are also left out of most models. In these cases, the decomposition products of the detritus and sediments as well as all soluble excretions go directly to the dissolved inorganic nutrient compartments. This in effect combines the suspended particulate and dissolved organic compartments into a single "unavailable" nutrient compartment which decays to produce available inorganic forms.

Nitrogen models also differ in the forms of inorganic nitrogen which are included, as well as in some of the processes modeled. For example, some models include only ammonia and nitrate, rather than the full oxidation sequence of ammonia to nitrite to nitrate. While most models include the nitrification reactions, only a few include denitrification. Also, only a few models include nitrogen-fixation by blue-green algae.

Sediments and particulate organic detritus are often modeled as single compartments, rather than having a separate compartment for each nutrient. In this case, the corresponding compartments for each nutrient are determined from the product of the total sediment and detritus concentrations and the stoichiometric ratios for each nutrient. The stoichiometric ratios are generally the same as those used for algae (see Section 6.3 of Chapter 6) so that mass is conserved during nutrient recycling.

Table 5-1 presents a comparison of the various nutrient forms included in several models. Transformation processes and the corresponding rate coefficients for each specific nutrient are discussed below, along with model formulations for nutrient uptake, excretion, and sediment release. Formulations for plankton mortality and zooplankton grazing are discussed in Chapters 6 and 7. Settling formulations for particulate organic detritus are essentially the same as the simplest formulations used for phytoplankton settling described in Chapter 6 (i.e., the settling rate equals the user-specified settling velocity divided by the depth of the model segment).

5.4 TEMPERATURE EFFECTS

Temperature influences the rates of all of the nutrient transformation processes discussed above. All of the first-order rate coefficients in Equations (5-1) through (5-4) are therefore temperature dependent. Almost all models use the exponential Arrhenius or van't Hoff relationship to describe these effects. A reference temperature of 20°C is usually assumed when specifying each rate coefficient, resulting in the following equation:

TABLE 5-1. COMPARISON OF NUTRIENT MODELS

Model (Author)	Nutrients Modeled				Nutrient Forms							Inorganic Nitrogen Forms				References
	C	N	P	Si	Dislvd. Inorg.	Dislvd. Organic	Partic. Organic	Sedi- ments	Algae	Zoo- plankton	Other Organisms	NH ₃	NO ₂	NO ₃	Total Avail	
AQUA-IV		X	X		X	N	X	X	X	X		X	X	X		Baca & Arnett (1976)
CE-QUAL-R1	X	X	X		X		X	X	X	X	X	X	X	X		WES (EWQOS) (1982)
CLEAN	X	X	X		X	X	X	X	X	X	X				X	Bloomfield <i>et al.</i> (1973)
CLEANER	X	X	X		X	X	X	X	X	X	X				X	Scavia & Park (1976)
MS.CLEANER	X	X	X	X	X	X	X	X	X	X	X				X	Park <i>et al.</i> (1980)
DEM		X	X		X			X*	X			X	X	X		Feigner & Harris (1970)
DOSAG3		X	X		X			X*	X			X	X	X		Duke & Masch (1973)
EAM	X	X	X	X	X		X	X	X	X	X	X	X	X		Tetra Tech (1979, 1980)
ESTECO	X	X	X		X		X	X	X	X	X	X	X	X		Brandes & Masch (1977)
EXPLORE-1	X	X	X		X		X	P	X	X		X	X	X		Baca <i>et al.</i> (1973)
HSPF	X	X	X		X		X	X*	X	X		X	X	X		Johanson <i>et al.</i> (1980)
LAKECO	X	X	X		X		X	X	X	X	X	X	X	X		Chen & Orlob (1975)
MIT Network		X			X	N	X		X	X		X	X	X		Harleman <i>et al.</i> (1977)
QUAL-II		X	X		X			X*	X			X	X	X		Roesner <i>et al.</i> (1981)
RECEIV-II		X	X		X				X			X	X	X		Raytheon (1974)
SSAM IV		X	X		X				X			X		X		Grenney & Kraszewski (1981)
WASP	X	X	X	X	X	X	X	X	X	X		X		X		Di Toro <i>et al.</i> (1981)
WQRRS	X	X	X		X		X	X	X	X	X	X	X	X		Smith (1978)
Bierman		X	X	X	X		X		X	X					X	Bierman <i>et al.</i> (1980)
Canale		X	X	X	X	X	X		X	X		X		X		Canale <i>et al.</i> (1975, 1976)
Jorgensen		X	X		X		X	X	X	X	X				X	Jorgensen (1976)
Lehman	X	X	X		X				X						X	Lehman <i>et al.</i> (1975)
Nyholm		X	X		X		X	X	X						X	Nyholm (1978)
Scavia	X	X	X		X	N	X	X	X	X		X		X		Scavia <i>et al.</i> (1976)

*Specify flux.

$$K_T = K_{20} \theta^{(T-20)}$$

5-5)

where K_T = rate coefficient at temperature T, 1/time

T = temperature, °C

K_{20} = rate coefficient at 20°C, 1/time

θ = temperature adjustment coefficient

This relationship is derived in Section 3.3 of Chapter 3.

A few models use different temperature adjustment formulations. For example, Canale (1976) uses a linear relationship and Grenney and Kraszweski (1981) use a logistic equation as a temperature adjustment function.

5.5 CARBON TRANSFORMATIONS

Table 5-2 presents rate coefficients for carbon decay processes along with the corresponding temperature adjustment factors. As shown in the table, these coefficients have a broad range, indicating a lack of detailed process characterization. Process characterization has been neglected in carbon models since the relationship of carbon dynamics to water quality modeling has not been considered essential. In fact, most water quality models do not include carbon since it is not usually a limiting nutrient. In the Lake Erie version of WASP (Di Toro and Connolly, 1980), the rate of decay of particulate organic carbon to CO_2 has been further reduced by using a saturation relationship (Di Toro and Connolly, 1980). However, the decay rates in all other models are computed according to the first-order kinetics discussed above.

Most of the temperature adjustment factors in Table 5-2 range from 1.02 to 1.047, corresponding to Q_{10} values ranging between 1.2 and 1.6. The exception is the Lake Erie WASP model (Di Toro and Connolly, 1980), which uses a temperature correction factor of 1.08 ($Q_{10} = 2.16$) for decay of settled algae and sediment organic matter. Also, the decay rate constants for these compartments are generally higher than those used in other models.

TABLE 5-2. RATE COEFFICIENTS FOR CARBON TRANSFORMATIONS

POC \rightarrow CO ₂		SOC \rightarrow CO ₂		SA \rightarrow SOC		SA \rightarrow CO ₂		References
K	θ	K	θ	K	θ	K	θ	
0.1**	1.04	0.00025	1.08	0.02	1.08	0.02	1.08	Di Toro & Connolly (1980)
0.05	1.045							O'Connor <i>et al.</i> (1981)
0.001	1.02	0.001	1.02					Chen & Orlob (1972, 1975)
0.003	1.020	0.0015	1.047					Tetra Tech (1980)
0.02	1.020	0.001	1.020					Bowie <i>et al.</i> (1980)
0.1	1.047	0.0015	1.047					Porcella <i>et al.</i> (1983)
0.005-0.05***	1.02-1.04***	0.001-0.01***	1.02-1.04***					Smith (1978)
0.001-0.02***	1.040***	0.001-0.02***	1.040***					Brandes (1976)

*Abbreviations are defined as follows:

POC - Particulate Organic Carbon

CO₂ - Carbon Dioxide

SOC - Sediment Organic Carbon

SA - Settled Algae

**This rate is multiplied by an oxygen limitation factor, $\frac{O_2}{K_1 + O_2}$, where K_1 is a half-saturation constant for oxygen.

***Model documentation values.

5.6 NITROGEN TRANSFORMATIONS

Nitrogen dynamics are modeled in a considerably more complex manner than carbon because of their substantial biogeochemical role, important oxidation-reduction reactions, and because other important water quality variables such as oxygen are affected by nitrogen. The processes that are simulated in water quality models include:

- Ammonification - release of ammonia due to decay processes (deamination, hydrolysis).
- Nitrification - oxidation of ammonia to nitrate (NO_3^-) directly (one-stage process) or to nitrite (NO_2^-) and then to nitrate (two-stage process). Nitrification is discussed in detail in Section 3.4 of Chapter 3 in reference to its effects on dissolved oxygen.
- Denitrification - reduction of nitrate to N_2 under anaerobic conditions. This process also produces N_2O (10 percent of total reduced), but since N_2O has not been shown to have an appreciable effect on water quality, N_2O production has not been modeled.
- Uptake - accumulation of inorganic nitrogen by plants during photosynthetic growth. Both ammonia and nitrate are accumulated, with preference for ammonia over oxidized forms, although not all models include this preference.
- Nitrogen fixation - reduction of N_2 to ammoniated compounds. Nitrogen fixation by blue-green algae is an important external input of nitrogen accumulation in waterbodies that materially affects nitrogen dynamics. However, uptake of inorganic ions takes precedence over nitrogen fixation.

In addition to the above processes, unionized ammonia can play a significant role as a toxicant depending on the ammonia concentration, pH, and temperature.

Table 5-3 presents rate coefficients for the major nitrogen decay and abiotic transformation processes along with the corresponding temperature adjustment factors. The decay processes shown include breakdown of complex organic compounds (particulate organic nitrogen, PON) to simpler organics (dissolved organic nitrogen, DON) or to ammonia, the breakdown of sediment nitrogen to ammonia, and the oxidation of ammonia to nitrate. Rate constants for ammonia decay to nitrite and then to nitrate or from ammonia to nitrate directly are approximately commensurate as an overall rate process. The rate coefficients for some of the decay processes in some versions of WASP are further reduced by saturation kinetics (Di Toro and Connolly, 1980; Di Toro and Matystik, 1980; Thomann and Fitzpatrick, 1982; O'Connor et al., 1981). For example, the decay of particulate organic nitrogen to ammonia is reduced as chlorophyll a decreases, and the nitrification rate is reduced as dissolved oxygen decreases, according to saturation kinetics.

The temperature adjustment factors have a wide range of values, indicating some uncertainty in this coefficient. The Q_{10} values generally range from 1.2 to 2.4, but with one value as high as 3.7.

5.6.1 Denitrification and Nitrogen Fixation

Both of these processes affect the mass balance of nitrogen because nitrogen is transported to (denitrification) or from (nitrogen fixation) the atmosphere rather than recycling within the water. Although both processes have been shown to be important in certain aquatic environments, denitrification is not commonly included in models. HSPF (Johanson et al., 1980), CE-QUAL-R1 (WES, 1982), Jorgensen (1976), AQUA-IV (Baca and Arnett, 1976), and some versions of WASP (Di Toro and Connolly, 1980; Thomann and Fitzpatrick, 1982; O'Connor et al., 1981) include denitrification.

TABLE 5-3. RATE COEFFICIENTS FOR NITROGEN TRANSFORMATIONS

PON → DON		DON → NH ₃		PON → NH ₃		NH ₃ → NO ₂		NH ₃ → NO ₃		NO ₂ → NO ₃		SEDN → NH ₃		References
K	θ	K	θ	K	θ	K	θ	K	θ	K	θ	K	θ	
Calibration Values														
				0.035	(linear)			0.04	(linear)					Thomann <i>et al.</i> (1975)
				0.03**	1.08									Thomann <i>et al.</i> (1979)
				0.03***	1.08			0.12***	1.08			0.0025	1.08	Di Toro & Connolly (1980)
				0.03***	1.08			0.20	1.08					Di Toro & Matystik (1980)
				0.075	1.08			0.09-0.13***	1.08			0.0004	1.08	Thomann & Fitzpatrick (1982)
								0.025***	1.08					O'Connor <i>et al.</i> (1981)
				0.14	(linear)									Salas & Thomann (1978)
				0.001	1.02	0.003-0.03	1.02			0.09	1.02	0.001	1.02	Chen & Orlob (1972, 1975)
		0.020	(linear)	0.020	(linear)			0.060	(linear)					Scavia <i>et al.</i> (1976)
		0.020	(linear)	0.020	(linear)			0.1	(linear)					Scavia (1980)
		0.02	1.020	0.02	1.020			0.1	1.020					Bowie <i>et al.</i> (1980)
		0.02	(linear)	0.024	(linear)			0.16	(linear)					Canale <i>et al.</i> (1976)
				0.003	1.020	0.02	1.047			0.25	1.047	0.0015	1.047	Tetra Tech (1980)
				0.1	1.047	0.02	1.047			0.25	1.047	0.0015	1.047	Porcella <i>et al.</i> (1983)
				0.01**	NI							0.95-1.8***	1.14	Nyholm (1978)
				0.005**	1.08									Bierman <i>et al.</i> (1980)
				0.1**	1.02									Jorgensen (1976)
				0.2**	1.072									Jorgensen <i>et al.</i> (1978)

(continued)

TABLE 5-3. (continued)

PON + DON	DON + NH ₃	PON + NH ₃	NH ₃ + NO ₂	NH ₃ + NO ₃	NO ₂ + NO ₃	SEDN + NH ₃	References
K θ	K θ	K θ	K θ	K θ	K θ	K θ	
<u>Model Documentation Values</u>							
	0.1-0.4	NI	0.1-0.5	NI	5.-10.	NI	Baca <i>et al.</i> (1973)
	0.02-0.04	1.02-1.09	0.1-0.5	1.02-1.09	3.-10.	1.02-1.09	Baca & Arnett (1976)
			0.1-0.5	1.047	0.5-2.0	1.047	Duke & Masch (1973)
			0.1-0.5	1.047	0.5-20	1.047	Roesner <i>et al.</i> (1978)
	0.005-0.05	1.02-1.04	0.05-0.2	1.02-1.03	0.2-0.5	1.02-1.03	Smith (1978)
	0.001-0.02	1.040	0.05-0.2	1.02	0.2-0.5	1.02	Brandes (1976)
				0.04-3.0 (logistic)			Grenney & Kraszewski (1981)
				0.001-1.3****	NI		Collins & Wlosinski (1983)

*Abbreviations are defined as follows:

NI - No Information
 PON - Particulate Organic Nitrogen
 DON - Dissolved Organic Nitrogen
 SEDN - Sediment Organic Nitrogen

**Unavailable nitrogen decaying to algal-available nitrogen.

***Di Toro & Connolly (1980) and Di Toro & Matystik (1980) multiply the PON NH₃ rate by a chlorophyll limitation factor, $\frac{\text{Chl } a}{K_1 + \text{Chl } a}$, where K₁ is half-saturation constant = 5.0 µg Chl a/l.

Di Toro & Connolly (1980) and Thomann & Fitzpatrick (1982) multiply the NH₃ NO₃ rate by an oxygen limitation factor, $\frac{O_2}{K_2 + O_2}$, where K₂ is a half-saturation constant = 2.0 mgO₂/l.

O'Connor *et al.* (1981) multiply the NH₃ NO₃ rate by an oxygen limitation factor, $\frac{O_2}{K_3 + O_2}$, where K₃ is a half-saturation constant = 0.5 mgO₂/l.

Nyholm (1978) uses a sediment release constant which is multiplied by the total sedimentation rate of algae and detritus.

****Literature value.

Denitrification rates and the corresponding temperature adjustment coefficients are listed in Table 5-4. The decay rates for the WASP model are further modified according to a saturation type relationship based on the dissolved oxygen concentration. The rate decreases rapidly as O_2 increases above 0.01 mg/l. This rate would be equivalent to that of Jorgensen (1976) when $O_2 = 5$ mg/l. This indicates disagreement in conceptualization of the process or in its quantitative response between the two models. Sediment nitrate denitrification helps decrease the gradient of the sediment oxygen demand (SOD) and may lead to a reduced requirement for SOD (see Chapter 3.5; also, Di Toro, 1984).

Nitrogen fixation by blue-green algae is modeled by assuming that growth is not limited by nitrogen and that nitrogen fixation makes up for all nitrogen requirements which cannot be satisfied by ammonia and nitrate. Some type of saturation relationship is typically used to partition the nitrogen requirements between nitrogen fixation and uptake of ammonia and nitrate. The major features of these relationships are as follows: 1) no fixation occurs when ammonia plus nitrate are above some critical threshold concentration; 2) for concentrations below the threshold, nitrogen fixation increases as ammonia and nitrate decrease; and 3) when ammonia and nitrate become very low, all of the nitrogen requirements are supplied by fixation. Nitrogen fixation is included in the EAM (Tetra Tech, 1979), Scavia et al. (1976), Canale et al. (1976), and Bierman et al. (1980) models.

5.6.2 Unionized Ammonia

Although nitrogen is an important nutrient required by microorganisms, plants, and animals, certain forms such as unionized ammonia (NH_3) can be toxic. Unionized ammonia is toxic to fish at fairly low concentrations. For example, water quality criteria ranging from 0.0015 to 0.12 mg N/l for the 30-day average concentration have been suggested (USEPA, 1984). This range exists because the biological response varies at different temperature and pH values.

Both analytical measurement techniques and most model formulations for ammonia are based on total ammonia:

TABLE 5-4. RATE COEFFICIENTS FOR DENITRIFICATION

Nitrate → Nitrogen Gas		References
K	θ	
0.1*	1.045	Di Toro & Connolly (1980)
0.1**	1.045	Di Toro & Connolly (1980)
0.09*	1.045	Thomann & Fitzpatrick (1982)
0.1*	1.045	O'Connor <u>et al.</u> (1981)
0.002	No Information	Jorgensen (1976)
0.02-0.03	No Information	Jorgensen <u>et al.</u> (1978)
0.-1.0***	1.02-1.09***	Baca & Arnett (1976)

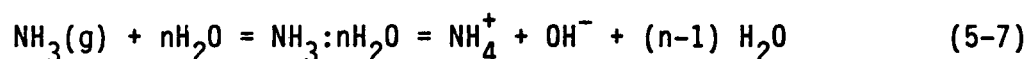
*This rate is multiplied by an oxygen limitation factor, $\frac{K_1}{K_1 + O_2}$, where K_1 is a half-saturation constant = 0.1mgO₂/l.

**The same rate applies to sediment NO₃ denitrification.

***Model documentation values.

$$X = \text{total ammonia} = \text{NH}_3 + \text{NH}_4^+ \quad (5-6)$$

The concentrations of NH₃ and NH₄⁺ vary considerably over the range of pH and temperature found in natural waters, but each can be readily calculated assuming that equilibrium conditions exist (Stumm and Morgan, 1981). Unionized ammonia exists in equilibrium with ammonia ion and hydroxide ion (Emerson, et al., 1975):



The reaction occurs rapidly and is controlled largely by pH and temperature. Thus, unionized ammonia is calculated from the equilibrium expression:

$$K_i = \frac{(\text{NH}_4^+)(\text{OH}^-)}{(\text{NH}_3)(\text{H}_2\text{O})} = \frac{(\text{NH}_4^+)K_w}{(\text{NH}_3)(\text{H}^+)} \quad (5-8)$$

Rearranging and taking the negative logarithm:

$$\log \frac{(\text{NH}_4^+)}{(\text{NH}_3)} = \text{p}K_w - \text{p}K_i - \text{pH} \quad (5-9)$$

The quantity $\text{p}K_h$ is called the hydrolysis constant. Substituting and taking the inverse logarithms,

$$\left(\frac{X - \text{NH}_3}{\text{NH}_3} \right) = 10^{(\text{p}K_h - \text{pH})} = R \quad (5-10)$$

and solving for NH_3 ,

$$\text{NH}_3 = \frac{X}{1 + R} \quad (5-11)$$

Thurston et al., (1974) determined the temperature correction for the hydrolysis constant as follows:

$$\text{p}K_h = 0.09018 + 2729.92/T \quad (5-12)$$

where T = absolute temperature, $^{\circ}\text{K}$

Substituting this relationship into Equation 5-7, unionized ammonia in moles/liter becomes a function of measured ammonia, temperature, and pH. Most water quality models predict the concentration of measured ammonia (X) in units of weight/volume as a resultant of processes of nitrification, ammonification, respiration, and assimilation. For $\text{NH}_3\text{-N}$, there are 14,000 mg/mole and

$$\text{NH}_3\text{-N, mg/l} = \frac{14000(X)}{1 + R} \quad (5-13)$$

Although more cumbersome, a table of equilibrium values for unionized ammonia can be used in a model (e.g., USEPA, 1984). Figure 5-5 illustrates the relationship between pH, water temperature, and unionized ammonia.

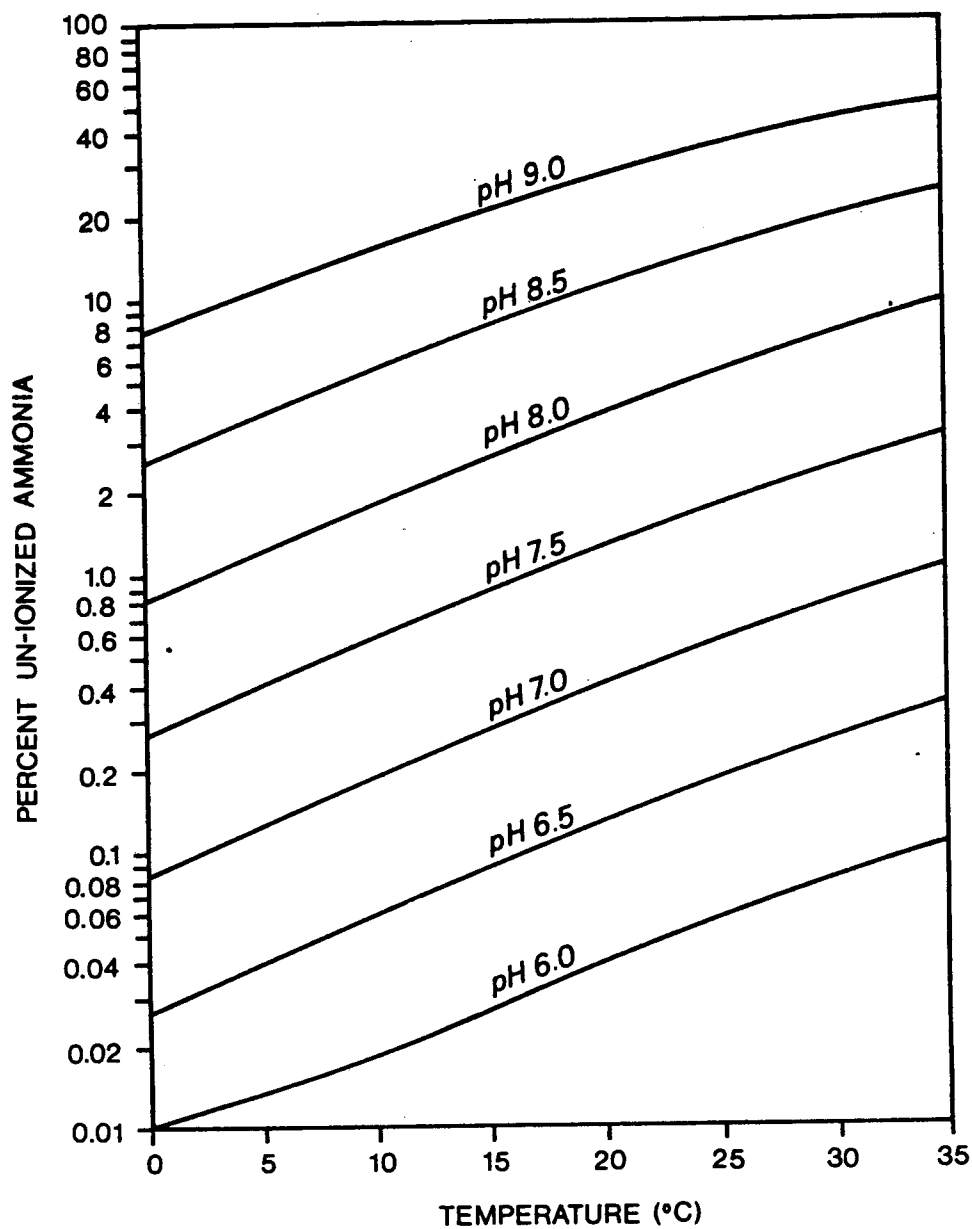


Figure 5-5. Effect of pH and temperature on unionized ammonia (from Willingham, 1976).

5.7 PHOSPHORUS TRANSFORMATIONS

Table 5-5 presents rate coefficients and temperature correction factors for the various phosphorus transformation processes included in water quality models. The transformations include the decay of particulate organic phosphorus (POP), sediment phosphorus (SEDP), and settled algae (SA) directly to $\text{PO}_4\text{-P}$ or into intermediate forms (dissolved organic phosphorus, DOP) before decaying to $\text{PO}_4\text{-P}$. The decay rates have a broad range, indicating some uncertainty in quantifying these processes. Similarly, there is a broad range in temperature coefficients, with a Q_{10} range from 1.2 to 2.4, except for a Q_{10} value of 3.7 for Nyholm (1978). Several of the WASP models adjust the phosphorus decay rates using a saturation equation based on algal biomass (Di Toro and Connolly, 1980; Di Toro and Matystik, 1980; Salisbury *et al.*, 1983; Thomann and Fitzpatrick, 1982). In the case where chlorophyll *a* is used to estimate algal biomass, the half-saturation constant is 5.0 g/l, and where carbon is used to estimate algal biomass, the value is 1.0 mgC/l.

5.8 SILICON TRANSFORMATIONS

Silicon can be limiting only for diatoms, so its biogeochemical cycle is simulated only when diatoms are modeled as a separate algal group. Diatoms are important because of their role in phytoplankton succession, their role in aquatic food chains, and their potential effects on water treatment plants. Table 5-6 presents decay rates and temperature adjustment coefficients for silicon. In contrast to the other nutrients, particulate and sediment silicon decay directly to dissolved inorganic silicon rather than passing through a dissolved organic phase. The range of the first-order decay rates for particulate silica decay is 0.003-0.1 (1/day). The temperature adjustment factor varies between 1.02 and 1.08, corresponding to a Q_{10} range of 1.2 to 2.2.

TABLE 5-5. RATE COEFFICIENTS FOR PHOSPHORUS TRANSFORMATIONS

POP → DOP		POP → PO ₄		DOP → PO ₄		SEDP → DOP		SEDP → PO ₄		Sediment DOP → PO ₄		Sediment SA → DOP		Sediment SA → PO ₄		References
K	θ	K	θ	K	θ	K	θ	K	θ	K	θ	K	θ	K	θ	
		0.14	(linear)													Thomann <i>et al.</i> (1975)
		0.03	1.08													Thomann <i>et al.</i> (1979)
		0.03**	1.08													Di Toro & Connolly (1980) Di Toro & Matystik (1980) Salisbury <i>et al.</i> (1983)
0.22**	1.08			0.22**	1.08	0.0004	1.08	0.0004	1.08	0.0004	1.08	0.02	1.08	0.02	1.08	Thomann & Fitzpatrick (1982)
		0.14	(linear)													Salas & Thomann (1978)
		0.001	1.02					0.001	1.02							Chen & Orlob (1972, 1975)
		0.02	(linear)													Scavia <i>et al.</i> (1976) Scavia (1980)
0.2	(linear)			0.2	(linear)											Canale <i>et al.</i> (1976)
		0.003	1.020					0.0015	1.047							Tetra Tech (1980)
		0.02	1.020					0.001	1.020							Bowie <i>et al.</i> (1980)
		0.1	1.047					0.0015	1.047							Porcella <i>et al.</i> (1983)
		0.1	1.14					1.0-1.7	1.14**							Nyholm (1978)
		0.005	1.08													Bierman <i>et al.</i> (1980)
		0.1	1.02					0.0018	1.02							Jorgensen (1976)
		0.5-0.8	1.072													Jorgensen <i>et al.</i> (1978)
		0.1-0.7***	1.02-1.09***					0.1-0.7***	1.02-1.09***							Baca <i>et al.</i> (1973)
		0.1-0.7***	1.02-1.09***													Baca & Arnett (1976)
		0.005-0.05***	1.02-1.04***					0.001-0.01***	1.02-1.04***							Smith (1978)
		0.001-0.02***	1.040***													Brandes (1976)

Abbreviations are defined as follows:

POP - Particulate Organic Phosphorus

DOP - Dissolved Organic Phosphorus

PO₄ - Phosphate

SEDP - Sediment Organic Phosphorus

SA - Settled Algae

**Di Toro & Connolly (1980), Di Toro & Matystik (1980) and Salisbury *et al.* (1983) multiply this rate by a chlorophyll limitation factor, $\frac{Chl\ a}{K_1 + Chl\ a}$, where K_1 is a half-saturation constant = 5.0 µg Chl a/l.

Thomann & Fitzpatrick (1982) multiply this rate by an algal carbon limitation factor, $\frac{Algal-C}{K_2 + Algal-C}$, where K_2 is a half-saturation constant = 1.0mgC/l.

Nyholm (1978) utilizes a sediment release constant which is multiplied by total sedimentation of algae and detritus.

***Model documentation values.

TABLE 5-6. RATE COEFFICIENTS FOR SILICA TRANSFORMATIONS

Particulate → Dissolved Silica Silica		Sediment → Dissolved Silica Silica		References
K	θ	K	θ	
0.0175	1.08			Thomann <u>et al.</u> (1979)
0.1	1.08			Di Toro & Connolly (1980)
0.04	(linear)			Scavia (1980)
0.03	(linear)			Canale <u>et al.</u> (1976)
0.003	1.020	0.005	1.047	Tetra Tech (1980)
0.01	1.020	0.001	1.020	Bowie <u>et al.</u> (1980)
0.04	1.047	0.0015	1.047	Porcella <u>et al.</u> (1983)
0.005	1.08			Bierman <u>et al.</u> (1980)

5.9 ALGAL UPTAKE

Two major approaches are used to simulate nutrient uptake by algae in water quality models. The most common method is the fixed stoichiometry approach in which the nutrient composition of the algae is assumed to remain constant. Under this assumption, the nutrient uptake rates are equal to the algal gross growth rate times the corresponding nutrient fractions of the algal cells:

$$V_s = \alpha_s \mu A \quad (5-14)$$

where V_s = uptake rate for nutrient S, mass/volume-time
 α_s = nutrient fraction of algal cells, mass nutrient/mass algae
 μ = gross growth rate of algae, 1/time
 A = algal concentration, mass/volume

This formulation is used in all fixed stoichiometry models. Typical values of the nutrient compositions of algae are given in Tables 6-2 to 6-4 of Chapter 6. Algal growth formulations and the corresponding model coefficients are discussed in Section 6.4 of Chapter 6.

The second approach to modeling nutrient uptake is the variable stoichiometry approach. In this method, the internal nutrient composition of the algal cells varies with time depending on the external nutrient concentrations in the water column and the relative rates of nutrient uptake and algal growth. The uptake rate depends on the difference between the internal nutrient concentration in the algal cells and the external concentration in the water. The internal concentration of each nutrient is assumed to range between a minimum stoichiometric requirement (called the minimum cell quota or subsistence quota) and some maximum internal concentration. In general, the uptake rate increases both as the external nutrient concentration increases and as the internal nutrient concentration decreases toward the minimum cell quota. However, the uptake rate decreases as the internal concentration approaches the maximum internal level, regardless of the external concentration in the water.

In contrast to fixed stoichiometry models, the uptake formulations used in variable stoichiometry models vary from model to model. Some models even use different formulations for different nutrients. Variable stoichiometry formulations for nutrient uptake are discussed in Section 6.4.4.3 of Chapter 6, since nutrient uptake is an integral part of the algal growth formulations in variable stoichiometry models. The major formulations are given in Equations (6-63) to (6-67).

5.9.1 Ammonia Preference Factors

Since algae use two forms of nitrogen, ammonia and nitrate, during uptake and growth, many models use ammonia preference factors in the uptake formulations to account for the fact that algae tend to preferentially uptake ammonia over nitrate. Ammonia preference factors are generally used in fixed stoichiometry models when both ammonia and nitrate are simulated. In this case, the uptake equations for ammonia and nitrate become:

$$V_{\text{NH}_3} = \beta_{\text{NH}_3} \alpha_N \mu A \quad (5-15)$$

and

$$V_{\text{NO}_3} = (1 - \beta_{\text{NH}_3}) \alpha_N \mu A \quad (5-16)$$

where V_{NH_3} = ammonia uptake rate, mass/volume-time

V_{NO_3} = nitrate uptake rate, mass/volume-time

β_{NH_3} = ammonia preference factor

α_N = nitrogen fraction of algal cells

Ammonia preference factors are generally not needed in variable stoichiometry models since separate formulations with different coefficients can be used to distinguish between ammonia and nitrate uptake rates.

The ammonia preference factor β_{NH_3} partitions the nitrogen uptake required for a given amount of algal growth between ammonia and nitrate. The preference factor can range from 0 to 1, with 1 corresponding to a

situation in which all the nitrogen requirements are obtained from ammonia uptake, and 0 corresponding to a situation in which all the nitrogen is obtained from nitrate. The value of the preference factor is generally a function of the ammonia and nitrate concentrations in the water.

The simplest form of the ammonia preference factor assumes there is no preference for either form of nitrogen and partitions the uptake according to the relative proportions of ammonia and nitrate in the water:

$$\beta_{\text{NH}_3} = \frac{\text{NH}_3}{\text{NH}_3 + \text{NO}_3} \quad (5-17)$$

where NH_3 = ammonia concentration, mass/volume

NO_3 = nitrate concentration, mass/volume

This approach is used in EXPLORE-1 (Baca et al., 1973), LAKECO (Chen and Orlob, 1975), WQRRS (Smith, 1978), CE-QUAL-R1 (WES, 1982), EAM (Tetra Tech, 1979), ESTECO (Brandes, 1976), and earlier versions of WASP (Thomann et al., 1975).

Other models which assume there is a preference for ammonia uptake have used the following formulations for the preference factor:

$$\beta_{\text{NH}_3} = \frac{\gamma_1 \text{NH}_3}{\gamma_1 \text{NH}_3 + \text{NO}_3} \quad (5-18)$$

$$\beta_{\text{NH}_3} = \frac{\text{NH}_3}{\gamma_2 + \text{NH}_3} \quad (5-19)$$

$$\beta_{\text{NH}_3} = \frac{\gamma_3 \text{NH}_3}{\gamma_3 \text{NH}_3 + (1 - \gamma_3) \text{NO}_3} \quad (5-20)$$

$$\beta_{\text{NH}_3} = \left(\frac{\text{NH}_3}{\text{NH}_3 + \gamma_4} \right) \left(\frac{\text{NO}_3}{\text{NO}_3 + \gamma_4} \right) + \left(\frac{\text{NH}_3}{\text{NH}_3 + \text{NO}_3} \right) \left(\frac{\gamma_4}{\gamma_4 + \text{NO}_3} \right) \quad (5-21)$$

where $\gamma_1, \gamma_2, \gamma_3, \gamma_4$ = coefficients in ammonia preference factor formulations

Equation (5-18) is used in SSAM IV (Grenney and Kraszewski, 1981) and Scavia et al. (1976), Equation (5-19) in an early Lake Erie WASP model by Di Toro et al. (1975), Equation (5-20) in AQUA-IV (Baca and Arnett, 1976) and Canale et al. (1976), and Equation (5-21) in more recent versions of WASP by Thomann and Fitzpatrick (1982) and O'Connor et al. (1981).

5.10 EXCRETION

Nutrient excretion by algae and zooplankton is one of the major components of nutrient recycling. In almost all models, nutrient excretion is modeled as the product of the respiration mass flux and the nutrient stoichiometry of the organisms. The equations for algal excretion and zooplankton excretion are:

$$e_{sa} = \alpha_{sa} r_a A \quad (5-22)$$

and

$$e_{sz} = \alpha_{sz} r_z Z \quad (5-23)$$

where e_{sa} = algal excretion rate of nutrient S, mass/volume-time
 e_{sz} = zooplankton excretion rate of nutrient S, mass/volume-time
 α_{sa} = nutrient fraction of algal cells, mass nutrient/mass algae
 α_{sz} = nutrient fraction of zooplankton, mass nutrient/mass zooplankton
 r_a = algal respiration rate, 1/time
 r_z = zooplankton respiration rate, 1/time
 A = algal concentration, mass/volume
 Z = zooplankton concentration, mass/volume

The excretion formulations for other organisms such as fish or benthic animals is the same as for zooplankton. Respiration rate formulations for algae and zooplankton are discussed in Section 6.5 (Chapter 6) and 7.4 (Chapter 7), respectively. The nutrient compositions of algae are presented in Tables 6-2 to 6-4 of Chapter 6. The nutrient compositions of zooplankton are typically assumed to be the same as for algae in fixed stoichiometry models so that nutrient mass is conserved as biomass cycles through the food web.

5.11 SEDIMENT RELEASE

Three major approaches have been used to simulate nutrient release from the sediments in water quality models. The simplest approach is to specify an areal flux from the bottom in the mass balance equations for dissolved nutrients. This technique is commonly used in river models and in models which do not dynamically simulate sediments as a separate constituent (e.g., QUAL-II (Roesner et al., 1981), DOSAG3 (Duke and Masch, 1973), and HSPF (Johanson et al., 1980)). Sediment release rates are highly site-specific, and are determined largely by model calibration of the dissolved nutrients.

The second approach is to model sediment nutrients as a dynamic pool using a mass balance equation such as Equation (5-4). In this method, nutrients are released according to a first-order decay rate:

$$R_s = \alpha_s K_{sed} Sed \quad (5-24)$$

where R_s = sediment release rate of nutrient S, mass/volume-time
 α_s = stoichiometric ratio of nutrient per mass organic sediment
 K_{sed} = organic sediment decay rate, 1/time
 Sed = concentration of organic sediment, mass/volume

The organic sediment pool increases as algae and suspended organic detritus settle to the bottom, and decreases as the sediment decomposes. This approach is used in LAKECO (Chen and Orlob, 1975), Chen et al. (1975), WQRRS (Smith, 1978), CE-QUAL-R1 (WES, 1982), EAM (Tetra Tech, 1979), and ESTECO (Brandes, 1976). In some models, a fraction of the settled particulates is assumed to be refractory and unavailable for mineralization.

The third approach to modeling sediment release uses a more complex mechanistic approach in which: 1) organic sediments undergo the same decay sequences as particulate organics in the water column but with the decay products going to the interstitial water rather than the overlying water, and 2) the nutrients in the interstitial waters diffuse to the overlying water at a rate depending on the concentration gradient between the

interstitial water and overlying water. This approach is used in some versions of WASP (e.g., Di Toro and Connolly, 1980; Thomann and Fitzpatrick, 1982). A few models also include denitrification in the transformation reactions.

Nyholm (1978) simulates sediment release dynamically without actually modeling sediments by assuming the release rates equal the product of a temperature dependent coefficient times the sedimentation rates of algal and detrital nutrients to the bottom.

5.12 SUMMARY

Carbon, nitrogen, phosphorus, and silicon are the major growth limiting nutrients included in water quality models. Nitrogen is also important because of the effects of nitrification on dissolved oxygen dynamics and because of ammonia toxicity. All nutrients recycle continuously in the water column between particulate and sediment forms, dissolved organic forms, dissolved inorganic forms, and biotic forms. The important processes are decomposition of organic particulates and sediments, decay of dissolved organic to inorganic forms, chemical transformations such as nitrification, photosynthetic uptake of dissolved inorganic forms, and soluble and particulate excretion by aquatic organisms. Denitrification and nitrogen fixation are also important in some situations.

First-order kinetics are used in almost all models to describe the various decay processes and transformations. The exponential Arrhenius or van't Hoff relationship is used to adjust the rate coefficients for temperature effects. Some of the processes are modified by Michaelis-Menten type saturation kinetics in a few models. Uptake and excretion are based on algal growth rates and algal and zooplankton respiration rates combined with the nutrient stoichiometries of the organisms. More complex formulations are used for nutrient uptake in variable stoichiometry models. Sediment release rates are usually modeled either by specifying a nutrient flux or modeling sediments as a nutrient pool subject to first-order decay. A few models use more complex formulations which include decay reactions in the

interstitial waters and diffusion between the interstitial waters in the sediment and the overlying water column.

5.13 REFERENCES

Baca, R.G., W.W. Waddel, C.R. Cole, A. Brandstetter, and D.B. Clearlock. 1973. EXPLORE-I: A River Basin Water Quality Model. Battelle, Inc., Pacific Northwest Laboratories, Richland, Washington.

Baca, R.G. and R.C. Arnett. 1976. A Limnological Model for Eutrophic Lakes and Impoundments. Battelle, Inc., Pacific Northwest Laboratories, Richland, Washington.

Bierman, V.J., Jr. 1976. Mathematical Model of the Selective Enhancement of Blue-Green Algae by Nutrient Enrichment. In: Modeling Biochemical Processes in Aquatic Ecosystems. R.P. Canale (ed.). Ann Arbor Science Publishers, Ann Arbor, Michigan. pp. 1-31.

Bierman, V.J., Jr., D.M. Dolan, E.F. Stoermer, J.E. Gannon, and V.E. Smith. 1980. The Development and Calibration of a Multi-Class Phytoplankton Model for Saginaw Bay, Lake Huron. Great Lakes Environmental Planning Study. Contribution No. 33. Great Lakes Basin Commission, Ann Arbor, Michigan.

Bloomfield, J.A., R. A. Park, D. Scavia, and C.S. Zahorcak. 1973. Aquatic Modeling in the Eastern Deciduous Forest Biome. U.S. International Biological Program. In: Modeling the Eutrophication Process. E.J. Middlebrook, D.H. Falkenberg, and T.E. Maloney, (eds.). Utah State University, Logan, Utah. pp. 139-158.

Bowie, G.L., C.W. Chen, and D.H. Dykstra. 1980. Lake Ontario Ecological Modeling, Phase III, Tetra Tech, Inc., Lafayette, California. For National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Ann Arbor, Michigan.

Brandes, R.J. 1976. An Aquatic Ecologic Model for Texas Bays and Estuaries. Water Resources Engineers, Inc., Austin, Texas. For the Texas Water Development Board, Austin, Texas.

Brandes, R.J. and F.D. Masch. 1977. ESTECO--Estuarine Aquatic Ecologic Model: Program Documentation and User's Manual. Water Resources Engineers, Inc., Austin, Texas. For the Texas Water Development Board, Austin, Texas.

Canale, R.P., L.M. Depalma, and A.H. Vogel. 1975. A Food Web Model for Lake Michigan. Part 2 - Model Formulation and Preliminary Verification. Tech. Report 43, Michigan Sea Grant Program, MICHU-SG-75-201.

Canale, R.P., L.M. Depalma, and A.H. Vogel. 1976. A Plankton-Based Food Web Model for Lake Michigan. In: Modeling Biochemical Processes in Aquatic Ecosystems. R.P. Canale (ed.). Ann Arbor Science Publishers, Ann Arbor, Michigan. pp. 33-74.

Chen, C.W. and G.T. Orlob. 1972. Ecologic Simulations of Aquatic Environments. Water Resources Engineers, Inc., Walnut Creek, California. For the Office of Water Resources Research.

Chen, C.W. and C.T. Orlob. 1975. Ecological Simulation for Aquatic Environments. In: Systems Analysis and Simulation in Ecology, Vol. 3. B.C. Patten (ed.). Academic Press, Inc., New York, New York. pp. 476-588.

Chen, C.W., M. Lorenzen, and D.J. Smith. 1975. A Comprehensive Water Quality-Ecological Model for Lake Ontario. Tetra Tech, Inc., Lafayette, California. For National Oceanic and Atmospheric Administration, Great Lakes Environmental Research Laboratory, Ann Arbor, Michigan.

Collins, C.D. and J.H. Wlosinski. 1983. Coefficients for Use in the U.S. Army Corps of Engineers Reservoir Model, CE-QUAL-R1. U.S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, Mississippi.

Di Toro, D.M., D.J. O'Connor, R.V. Thomann, and J.L. Mancini. 1975. Phytoplankton-Zooplankton Nutrient Interaction Model for Western Lake Erie. In: Systems Analysis and Simulation in Ecology, Vol. III. B.C. Patton (ed.). Academic Press, Inc., New York, New York. 423 pp.

Di Toro, D.M. and J.P. Connolly. 1980. Mathematical Models of Water Quality in Large Lakes. Part II: Lake Erie. U.S. Environmental Protection Agency, Ecological Research Series. EPA-600/3-3-80-065.

Di Toro, D.M. and W.F. Matystik, Jr. 1980. Mathematical Models of Water Quality in Large Lakes. Part I: Lake Huron and Saginaw Bay. U.S. Environmental Protection Agency, Ecological Research Series. EPA-600/3-80-056.

Duke, J.H., Jr. and F.D. Masch. 1973. Computer Program Documentation for the Stream Quality Model DOSAG3, Vol. I. Water Resources Engineers, Inc., Austin, Texas. For U.S. Environmental Protection Agency, Systems Development Branch, Washington, D.C.

Emerson, K., R.C. Russo, R.E. Lund, and R.V. Thurston. 1975. Aqueous Ammonia Equilibrium Calculations: Effect of pH and Temperature. J. Fish. Res. Board Can., 32(12):2379-2383.

Feigner, K.D. and H. Harris. 1970. FWQA Dynamic Estuary Model, Documentation Report. U.S.D.I., F.W.Q.A., Washington, D.C.

Grenney, W.J. and A.K. Kraszewski. 1981. Description and Application of the Stream Simulation and Assessment Model: Version IV (SSAM IV). Instream Flow Information Paper. U.S. Fish and Wildlife Service, Fort Collins, Colorado, Cooperative Instream Flow Service Group.

Harleman, D.R.F., J.E. Dailey, M.L. Thatcher, T.O. Najarian, D.N. Brocard, and R.A. Ferrara. 1977. User's Manual for the M.I.T. Transient Water Quality Network Model--Including Nitrogen-Cycle Dynamics for Rivers and Estuaries. R.M. Parsons Laboratory for Water Resources and Hydrodynamics,

Massachusetts Institute of Technology, Cambridge, Massachusetts. For U.S. Environmental Protection Agency, Corvallis, Oregon. EPA-600/3-77-010.

Johanson, R.C., J.C. Imhoff, and H.H. Davis. 1980. User's Manual for Hydrological Simulation Program - Fortran (HSPF). Hydrocomp, Inc., Mountain View, California. For U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/9-80-015.

Jorgensen, S.E. 1976. A Eutrophication Model for a Lake. *Ecol. Modeling*, 2:147-165.

Jorgensen, S.E., H. Mejer, and M. Friis. 1978. Examination of a Lake Model. *Ecol. Modeling*, 4:253-278.

Lehman, J.T., D.B. Botkin, and G.E. Likens. 1975. The Assumptions and Rationales of a Computer Model of Phytoplankton Population Dynamics. *Limnol. and Oceanogr.*, 20(3):343-364.

Nyholm, N. 1978. A Simulation Model for Phytoplankton Growth and Nutrient Cycling in Eutrophic, Shallow Lakes. *Ecol. Modeling*, 4:279-310.

O'Connor, D.J., J.L. Mancini, and J.R. Guerriero. 1981. Evaluation of Factors Influencing the Temporal Variation of Dissolved Oxygen in the New York Bight, Phase II. Manhattan College, Bronx, New York.

Park, R.A., C.D. Collins, C.I. Connolly, J.R. Albanese, and B.B. MacLeod. 1980. Documentation of the Aquatic Ecosystem Model MS.CLEANER. Rensselaer Polytechnic Institute, Center for Ecological Modeling, Troy, New York. For U.S. Environmental Protection Agency, Environmental Research Laboratory, Office of Research and Development, Athens, Georgia.

Porcella, D.B., T.M. Grieb, G.L. Bowie, T.C. Ginn, and M.W. Lorenzen. 1983. Assessment Methodology for New Cooling Lakes, Vol. 1: Methodology to Assess Multiple Uses for New Cooling Lakes. Tetra Tech, Inc., Lafayette, California. For Electric Power Research Institute. Report EPRI EA-2059.

Raytheon Company, Oceanographic & Environmental Services. 1974. New England River Basins Modeling Project, Vol. III - Documentation Report, Part 1 - RECEIV-II Water Quantity and Quality Model. For Office of Water Programs, U.S. Environmental Protection Agency, Washington, D.C.

Roesner, L.A., P.R. Giguere, and D.E. Evenson. 1981. Computer Program Documentation for the Stream Quality Model QUAL-II. U.S. Environmental Protection Agency, Athens, Georgia. EPA 600/9-81-014.

Salas, H.J. and R.V. Thomann. 1978. A Steady-State Phytoplankton Model of Chesapeake Bay. *Journal WPCF*, 50(12):2752-2770.

Salisbury, D.K., J.V. DePinto, and T.C. Young. 1983. Impact of Algal-Available Phosphorus on Lake Erie Water Quality: Mathematical Modeling. For U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth, Minnesota.

Scavia, D., B.J. Eadie, and A. Robertson. 1976. An Ecological Model for Lake Ontario - Model Formulation, Calibration, and Preliminary Evaluation. Natl. Ocean. and Atmos. Admin., Boulder, Colorado. NOAA Tech. Rept. ERL 371-GLERL 12.

Scavia, D. and R.A. Park. 1976. Documentation of Selected Constructs and Parameter Values in the Aquatic Model CLEANER. Ecol. Modeling, 2:33-58.

Scavia, D. 1980. An Ecological Model of Lake Ontario. Ecol. Modeling, 8:49-78.

Smith, D.I. 1978. Water Quality for River-Reservoir Systems. Resource Management Associates, Inc., Lafayette, California. For U.S. Army Corps of Engineers, Hydrologic Engineering Center (HEC), Davis, California. pp 210.

Stumm, W. and J.J. Morgan. 1970 (First Edition). 1981 (Second Edition). Wiley-Interscience. New York, New York. 583 pp., 780 pp.

Tetra Tech, Inc. 1979. Methodology for Evaluation of Multiple Power Plant Cooling System Effects, Volume II. Technical Basis for Computations. Tetra Tech, Inc., Lafayette, California. For Electric Power Research Institute. Report EPRI EA-1111.

Tetra Tech, Inc. 1980. Methodology for Evaluation of Multiple Power Plant Cooling System Effects, Volume V. Methodology Application to Prototype - Cayuga Lake. Tetra Tech, Inc., Lafayette, California. For Electric Power Research Institute. Report EPRI EA-1111.

Thomann, R.V., D.M. Di Toro, R.P. Winfield, and D.J. O'Connor. 1975. Mathematical Modeling of Phytoplankton in Lake Ontario, Part 1. Model Development and Verification. Manhattan College, Bronx, New York. For U.S. Environmental Protection Agency, Corvallis, Oregon. EPA-600/3-75-005.

Thomann, R.V., J. Segna, and R. Winfield. 1979. Verification Analysis of Lake Ontario and Rochester Embayment Three-Dimensional Eutrophication Models. Manhattan College, Bronx, New York. For U.S. Environmental Protection Agency, Office of Research and Development.

Thomann, R.V. and J.J. Fitzpatrick. 1982. Calibration and Verification of a Mathematical Model of the Eutrophication of the Potomac Estuary. Government of the District of Columbia, Washington, D.C.

Thurston, R.V., R.C. Russo, and K. Emerson. 1974. Aqueous Ammonia Equilibrium Calculations. Fisheries Bioassay Laboratory, Montana State Univ., Bozeman, Montana. Technical Report No. 74-1.

U.S. Environmental Protection Agency. 1984. Water Quality Criteria for the Protection of Aquatic Life and Its Uses - Ammonia. USEPA, Criteria and Standards. Washington, D.C.

WES (Waterways Experiment Station). 1982. CE-QUAL-R1: A Numerical One-Dimensional Model of Reservoir Water Quality, Users Manual. Environmental

and Water Quality Operational Studies (EWQOS), U.S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, Mississippi.

Willingham, W.T. 1976. Ammonia Toxicity. EPA 908/3-76-001.